

# Rheology and Self-Assembly of Carboxylated Cellulose Nanocrystals

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## ABSTRACT

The demand for biobased materials is ever increasing and one such material are cellulose nanocrystals (CNCs). CNCs are the crystalline regions of cellulose polymers which have had the amorphous regions chemically cleaved, some methods include acid hydrolysis or oxidation. The remaining nanoparticles have charged acid groups on the surface which allow them to remain suspended in water. They are useful in a variety of applications as emulsifiers, flow modifiers, etc. To understand the extent in which CNCs can be used, a thorough understanding of self-assembly and flow behaviour is required. The acid hydrolysis of cellulose using high concentration sulfuric acid is a common way to produce sulfated CNCs, the rheological properties of which have been well explored in published works<sup>1,2,3</sup>. However, the carboxylated cellulose nano crystals utilized in this study are produced commercially by Anomera, through oxidation using hydrogen peroxide. The only by-product of this process is water, this procedure is has much fewer harmful by products than the more common acid hydrolysis. However, the rheological properties of carboxylated CNCs have not been explored. In this work the viscosity and viscoelastic properties of carboxylated cellulose nanocrystals are examined to determine if there are major behavioural differences caused by the acid group on the surface. In suspension carboxylated CNCs exhibit self-assembly behaviour above a critical concentration where they orient themselves into chiral nematic structures called tactoids. As the concentration continues to increase the tactoids grow and begin to coalesce until they separate to form a liquid crystalline phase. The critical concentration is determined through the examination of phase separation at increasing concentrations. The onset of tactoid formation and tactoid evolution in reference to concentration is examined using polarized optical microscopy. A visible progression of tactoid size and coalescence is observed starting just above the determined critical concentration. This self-assembly also has an impact on rheology. At low concentrations the viscosity profile demonstrates shear thinning flow. As the concentration increases the overall viscosity of the suspensions increases and shear thinning behaviour intensifies. Once a significant amount of the suspension has phase separated the suspensions start to demonstrate “three-region” flow behaviour. Three-region flow is characterized by three distinct flow behaviours along a range of shear rates. Region one is at low shear rates where flow is shear thinning. Region two occurs as shear rate increases and the interactions between particles in the liquid crystalline phase

break apart causing a hitch in the viscosity profile where the flow behaviour becomes more Newtonian. Region three occurs once interactions between particles have completely broken and the particles have aligned in the direction of shear, the flow behaviour returns to shear thinning at high shear rates. Interestingly, the onset of three-region flow behaviour does not correspond perfectly with the critical concentration so the presence of a few tactoids is not enough to alter the flow behaviour and a larger portion needs phase separated for the behaviour to change. This behaviour is in line with the literature focused on sulfated CNCs, where three-region flow is also visible in concentrations where phase separation occurs<sup>1,2,3</sup>. At even high concentrations kinetic arrest occurs which results in the CNCs showing purely shear thinning behaviour. Self-assembly is largely dependent on the surface charge of the CNCs. This work demonstrates that an increasing surface charge decreases interactions between particles which is evident in the overall lower viscosity at the same concentrations and the onset of phase separation, and by extension three-region flow behaviour, occurring at higher concentrations.

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